Appendix B
Review of Chemical Kinetics

If you have taken *Chemistry 217: Chemical Principles I* and *Chemistry 218: Chemical Principles II* from Athabasca University, you will find it helpful to reread Chapter 13 in *Chemistry: Molecules, Matter, and Change*, 4th ed., by Jones and Atkins. The following is a brief review of the basic chemical kinetics you will need to complete *Chemistry 350: Organic Chemistry I*.

The rate of a reaction is expressed as changes in concentration per unit of time (for solutions, the units are M/s). This rate can be written as the appearance of a product or the disappearance of a reactant. For the reaction

$$A \xrightarrow{\quad} B,$$

$$\text{Rate} = \frac{-dA}{dt} = \frac{dB}{dt}.$$

The relationship between reaction rate and concentration is expressed by the "rate law." The general form of this rate law is

$$\text{Rate} = k[A]^X[B]^Y[C]^Z\ldots$$

for the general reaction

$$A + B + C\ldots \xrightarrow{\quad} \text{Products}$$

where k is the "rate constant, $X, Y, Z\ldots$ are the reaction orders and $A, B, C\ldots$ are the reactants. [**Note:** The rate law *cannot* be determined by the coefficients in the chemical equation. It is determined experimentally.] The rate constant is specific to the nature of each reaction and will vary only with a change in temperature. The order of a reaction can be determined by its rate law. Working through the examples in the table below will quickly clarify this point.

Rate law	**Order of "A"**	**Order of "B"**	**Order of "C"**	**Overall Order**
Rate = $k[A]$	1	0	0	1
Rate = $k[A][B]$	1	1	0	2
Rate = $k[A][B][C]$	1	1	1	3
Rate = $k[A]^2[B]$	2	1	0	3
Rate = $k[B]^2[C]^{1/2}$	0	2	0.5	2.5
Rate = $k[A]^2/[B]$	2	−1	0	1
Rate = $k[A][B]/[C]^2$	1	1	−2	0
Rate = $k[A][B]^2[C]^2$	1	2	2	5

As you can see, rate laws can become very complicated expressions. For this course, you will be primarily dealing with first-order, second-order and pseudo first-order reactions.

First-order Reactions

$$\text{Rate} = k[A],$$

or in integrated form,

$$\ln[A]_t = -kt + \ln[A]_0,$$

where $[A]_t$ is the concentration of A at time t, and $[A]_0$ is the initial concentration of A. You should note that a graph of $\ln[A]_t$ versus time (t) will give a straight line of slope $-k$.

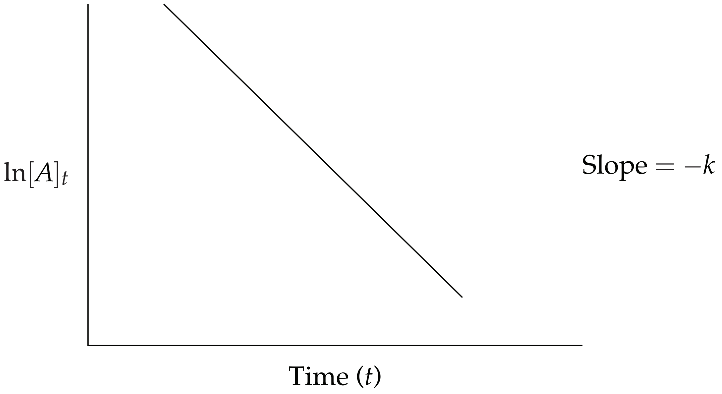

Figure B.1: Graph of $\ln[A]_t$ versus time (t)

First-order reactions also have a constant half-life ($t_{1/2}$) expressed by:

$$t_{1/2} = \frac{0.693}{k}.$$

Second-order Reactions

$$\text{Rate} = k[A]^2,$$

or in integrated form,

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt.$$

In this case, a graph of $\frac{1}{[A]_t}$ versus time (t) gives a straight line of slope k.

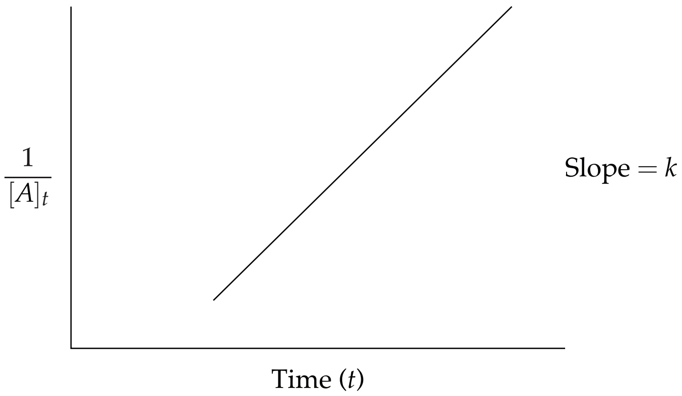

Figure B.2: Graph of $\frac{1}{[A]_t}$ versus time (t)

Pseudo First-order Reactions

If a higher order reaction has reactants that remain constant in concentration, it can be approximated as first-order for calculation purposes. For example, for the following second-order rate law:

$$\text{Rate} = k[A][B] \text{ (second-order)},$$

if $[B]$ remains relatively constant, as in a steady-state situation, then $[B]$ can be treated as a constant:

$$[B] \approx k'.$$

So,

$$\text{Rate} = k[A][B] \approx kk'[A] = K[A];$$

therefore,

$$\text{Rate} \approx K[A] \text{ (pseudo first-order)}$$

As long as $[B]$ is constant, we can simplify our calculations by treating this reaction as pseudo first-order.

Activation Energy

The minimum energy required for a reaction to occur is known as the activation energy (E_a), and can be determined by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_\text{a}}{RT}$$

where k is the rate constant, A is the frequency factor (a constant dependent on the nature of the reaction), T is temperature and R is the ideal gas constant.

A graph of $\ln k$ versus $\frac{1}{T}$ gives a straight line with slope $-\frac{E_\text{a}}{R}$.

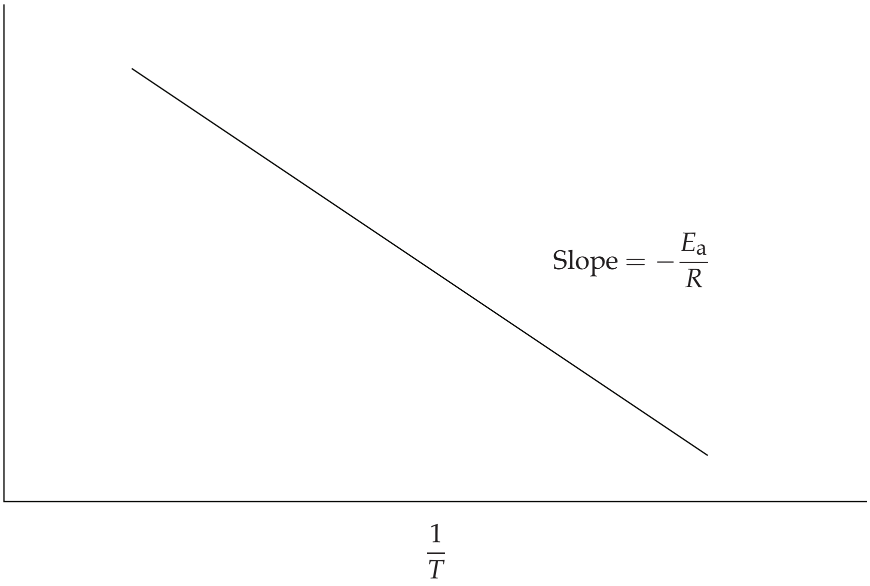

Figure B.3: Graph of $\ln k$ versus $\frac{1}{T}$

A catalyst can lower the activation energy of a reaction by providing a different reaction mechanism. Essentially, the catalyst speeds up the reaction without undergoing net chemical change itself.

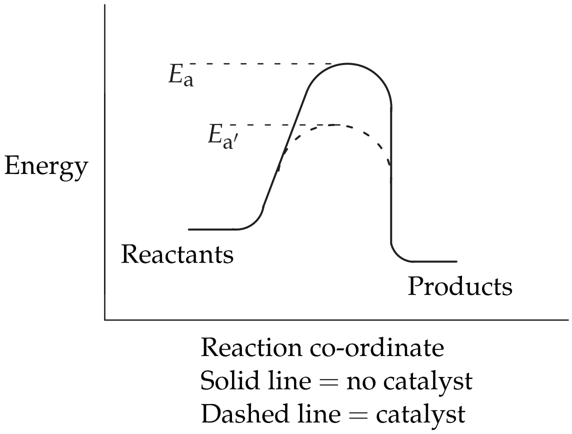

Figure B.4: Effect of a catalyst on activation energy

Reaction Mechanisms

A reaction mechanism is merely a series of elementary reactions that take place in sequence. The slowest reaction in this multistep sequence is the rate determining step. Consider the overall reaction:

$$A + 2 \longrightarrow D$$

The detailed mechanism of this reaction occurs the two steps shown below:

$$A + B \xrightleftharpoons{K} C$$

(fast)

$$C + B \xrightleftharpoons{k} D$$

(slow)

In the example above, the second reaction is the rate determining step, and the rate law will take the form of that step:

Rate = $k[C][B]$.

Note that from the equilibrium constant, K, in the first step, we can find an expression for $[C]$.

$$K = \frac{[C]}{[A][B]} \text{ or } [C] = K[A][B].$$

If we substitute this value for $[C]$ in the rate law dictated by the rate determining step, we can write an expression for the rate law based on only the reactants (i.e., not including any of the intermediates, such as C):

Rate = $k[C][B] = kK[A][B][B] = kK[A][B]^2$.